

Efficiency of isothermal molecular machines at maximum power

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We derive upper and lower bounds for the efficiency of an isothermal molecular machine operating at maximum power. The upper bound is reached when the activated state is close to the fueling or reactant state (Eyring-like), while the lower bound is reached when the activated state is close to the product state (Kramers-like).

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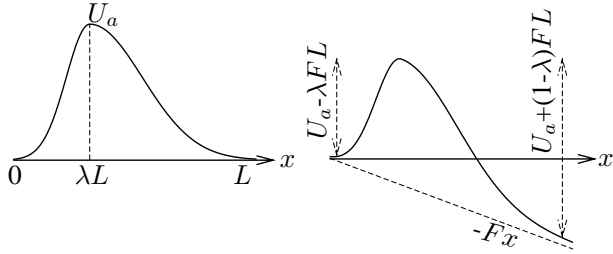


FIG. 1. Schematic free energy potential $U_0(x)$ for a two-state molecular engine described by a reaction coordinate x under the net load force $F = F_1 - F_2 \geq 0$.

According to thermodynamics, different forms of work can be transformed into one another, with an efficiency of at most 100% [1]. This lossless limit is achieved with a reversible process, i.e., an infinitely slow process. The corresponding power output is therefore zero and thus of limited interest from a practical standpoint. One of the early discussions about efficiency at *finite power* is attributed to Moritz von Jacobi around 1840. He realized that the output power of an electrical device operating in the linear response regime is maximum when the internal and external resistors are the same, yielding an efficiency of 50%. The Jacobi theorem can easily be reproduced in the much more general context of *linear* irreversible thermodynamics: in any engine operating in the linear response regime, maximum power is achieved when the loading force is equal to half of the stopping force; the corresponding efficiency (output power over input power) is equal to 1/2. A similar result has been proven for the transformation of heat into work, where the maximum efficiency, the Carnot efficiency, is again achieved under reversible operation, with zero power output. In the regime of linear response the efficiency at maximum power is again 50% of the Carnot efficiency [2]. More recently, in this latter case various explicit results, including bounds for efficiency at maximum power, have also been obtained in the *nonlinear* regime [3–11]. In the present paper we show that similar results can be derived for *isothermal* molecular machines [12, 13].

Generic model for a molecular motor. We first consider a generic model for a molecular motor, namely a two-state machine operating along a one-dimensional reaction coordinate, see Fig. 1. The states correspond to two minima of an appropriate free energy landscape. While a physical energy landscape is expected to be very complicated and high-dimensional, the thermally activated transitions between the two states will typically follow a preferred pathway that connects these states via the lowest lying saddle point, the so-called activated state. One can project the motion on this pathway and introduce a one-dimensional reaction coordinate x with corresponding effective free energy potential $U_0(x)$. The two “rest” states of the machine, that is, the minima in the absence of external forces, correspond to, say, locations $x = 0$ and $x = L$. The activated state lies at an intermediate position $x_a = \lambda L$, $0 \leq \lambda \leq 1$. In the unperturbed phase there are no net transitions, and the states 1 and 2 have the same baseline potential value, $U_0(0) = U_0(L) = 0$. The potential has a maximum $U_a = U_0(\lambda L)$ at the activated state, whose value is typically much larger than the thermal energy $\beta^{-1} = k_B T$ (T being the temperature and k_B the Boltzmann constant). In this rest state, the rates, k_0^+ from 1 to 2 and k_0^- from 2 to 1, are equal and given by an Arrhenius law, $k_0^+ = k_0^- \equiv k_0 = \kappa \exp(-\beta U_a)$. We assume a constant pre-exponential factor κ .

In the operational regime, that is, in the presence of external forces, states 1 and 2 can be identified as “fuel” (or “reactant”) and “product” states, respectively. To transform fuel into product, the machine is subject to a driving force F_1 which allows it to overcome an opposing but weaker loading force $-F_2$, $F_2 \leq F_1$. These forces can be of various physical origins, including chemical (differences in chemical potentials), electrical (internal or external electric fields) or mechanical (e.g., optical tweezers, atomic force microscope or optical rotational torque). The combined effect of driving and loading is a tilting of the potential towards the product state 2, $U(x) = U_0(x) - Fx$, with $F = F_1 - F_2 \geq 0$. In a transition from state 1 to state 2, a (scaled) input energy

$\epsilon_1 = \beta F_1 L$ is transformed into a (scaled) output energy $\epsilon_2 = \beta F_2 L$. The efficiency of this transformation is given by

$$\eta = \frac{\epsilon_2}{\epsilon_1} = \frac{F_2}{F_1}. \quad (1)$$

Its maximum value, $\eta = 1$, is reached when the loading force F_2 approaches the driving force F_1 , and the transition from 1 to 2 becomes infinitely slow. In this reversible lossless limit the power vanishes.

In the case of finite and in particular of maximum power, the location of the activated state plays a crucial role. For a so-called Eyring-like process [12] the activated state is very close to the fuel state 1, i.e., λ is close to zero. The perturbation $-Fx$ barely affects the height of the activation barrier that needs to be crossed to go from state 1 to 2. The rate also remains essentially unaffected, $k^+ \approx k_0$. However, a maximum barrier increase of FL occurs for the backward transition, resulting in a rate $k^- \approx k_0 \exp(-\beta FL)$ (assuming $FL \ll U_a$). On the other hand, in the Kramers-like scenario $\lambda \approx 1$ [12], $k^+ \approx k_0 \exp(\beta FL)$, while $k^- \approx k_0$ remains essentially unaffected. More generally, for a barrier at $x_a = \lambda L$, one has $k^+ = k_0 \exp(\lambda \epsilon)$ and $k^- = k_0 \exp[-(1-\lambda)\epsilon]$, where $\epsilon = \epsilon_1 - \epsilon_2 = \beta FL$ is the net energy loss or “net load.” This is proper thermodynamic force (net force divided by the temperature) that appears in the entropy production and is thus a measure of the distance from equilibrium [1].

With these explicit expressions for the rates, we turn to the output power Π given by the output energy ϵ_2 multiplied by its net rate of production, $\Pi = k\epsilon_2$, with $k = k^+ - k^- = k(\epsilon) = k_0 [e^{\lambda\epsilon} - e^{-(1-\lambda)\epsilon}]$. To specify the condition of maximum power we set $\partial\Pi/\partial\epsilon_2 = 0$, which yields the unique solution

$$\epsilon_2 = \frac{1 - e^{-\epsilon}}{\lambda(1 - e^{-\epsilon}) + e^{-\epsilon}} \quad (2)$$

$$= \epsilon + \left(\frac{1}{2} - \lambda\right)\epsilon^2 + \left(\frac{1}{6} - \lambda + \lambda^2\right)\epsilon^3 + O(\epsilon^4). \quad (3)$$

This result in Eq. (1) yields one of the central results of this paper, namely the efficiency at maximum power:

$$\eta^* = \frac{e^\epsilon - 1}{(\lambda\epsilon + 1)(e^\epsilon - 1) + \epsilon} \quad (4)$$

$$= \frac{1}{2} + \frac{1-2\lambda}{8}\epsilon + \frac{1-12\lambda+12\lambda^2}{96}\epsilon^2 + O(\epsilon^3). \quad (5)$$

We point to a number of revealing observations. The first term of the expansion (5) is the prediction of linear irreversible thermodynamics of efficiency at maximum power equal to $1/2$. The associated relation between the forces, $2F_2 = F_1$ is obtained from the first term in expansion (3), $\epsilon_2 = \epsilon \equiv \epsilon_1 - \epsilon_2$.

Turning to the next order corrections in Eqs. (3) and (5), the coefficients vanish in the symmetric case $\lambda = 1/2$,

reminiscent of a similar property for thermal machines [10]. Note also that the coefficient of the term proportional to ϵ in (5) goes from a maximum value $1/8$ at $\lambda = 0$ to the minimum value $-1/8$ for $\lambda = 1$, switching from positive to negative values at $\lambda = 1/2$, again reminiscent of an analogous feature in thermal machines [11]. The first two terms of the expansion (5) were also derived in [14], but the connection with the physically relevant parameter λ was not made (see, however, [15]).

The efficiency η^* at maximum power is a function of λ and ϵ . One easily verifies that η^* is a monotonically decreasing function of λ for given $\epsilon \geq 0$. The upper limit is the efficiency $\eta_E^* \equiv \eta^*(0, \epsilon) \leq 1$ of the extreme Eyring-like scenario, and the lower limit is the efficiency $0 \leq \eta_K^*(1, \epsilon) \equiv \eta^*$ of the extreme Kramers-like case:

$$\eta_K^* \equiv \frac{1 - e^{-\epsilon}}{1 - e^{-\epsilon} + \epsilon} \leq \eta^* \leq \frac{1 - e^{-\epsilon}}{1 - e^{-\epsilon} + \epsilon e^{-\epsilon}} \equiv \eta_E^*. \quad (6)$$

We next consider the ϵ dependence, starting with the variation of the bounds. The Eyring-like efficiency η_E^* increases monotonically from $1/2$ when $\epsilon \rightarrow 0$ to $\eta_E^* = 1$ when $\epsilon \rightarrow \infty$. The Kramers-like efficiency η_K^* decreases monotonically from $1/2$ when $\epsilon \rightarrow 0$ to $\eta_K^* = 0$ when $\epsilon \rightarrow \infty$. The variation of η^* between these bounds depends on λ . When $\lambda \geq 1/2$, η^* decreases monotonically from $1/2$ when $\epsilon = 0$ to 0 when $\epsilon \rightarrow \infty$. The system is in the product regime (Kramers-like), and η^* behaves much like the Kramers-like limit, never rising above the linear response value $1/2$ [dotted curve, short-dashed curve, and filled circles in Fig. 2(a)]. On the other hand, when $0 < \lambda \leq 1/2$ the system is in the fuel regime (Eyring-like), and η^* starts at $1/2$ when $\epsilon = 0$, rises to a unique maximum, and then decreases to 0 as $\epsilon \rightarrow \infty$ [long-dashed curve, solid curve, and open circles in Fig. 2(a)]. The “optimal” value of the efficiency at maximum power occurs at the net load value $\bar{\epsilon}$ which solves the transcendental equation obtained by setting the derivative of (4) with respect to ϵ equal to zero, $(1 - e^\epsilon)[\lambda(1 - e^\epsilon) - 1] = \bar{\epsilon}e^\epsilon$. Each point along the curve in the inset of Fig. 2(a) is associated with a different value of ϵ . High efficiencies at maximum power require the system to operate very near the fuel state. Thus, for instance, referring to the figure, the maximum of the $\lambda = 0.1$ curve (solid) is $\eta^* = 0.69$ and occurs when the net load is $\epsilon = 3.19$. A maximum efficiency of say $\eta^* = 0.9$ requires that the net load be $\epsilon = 5.68$ and that the motor operate at $\lambda = 0.016$.

We can repeat our analysis for $\epsilon \leq 0$, with net transitions going from state 2 to state 1. Indeed, many motors, including ATPase, can operate in reverse. The interchange of 1 and 2 corresponds to a replacement of λ by $1 - \lambda$. Hence the above theory indicates that, when considering both modes of operation, at least one of them has $\lambda \geq 1/2$, with a corresponding efficiency at maximum power less than 50%. For $\lambda = 1/2$ the engine works equally well at maximum power in forward and reverse modes, at 50% efficiency.

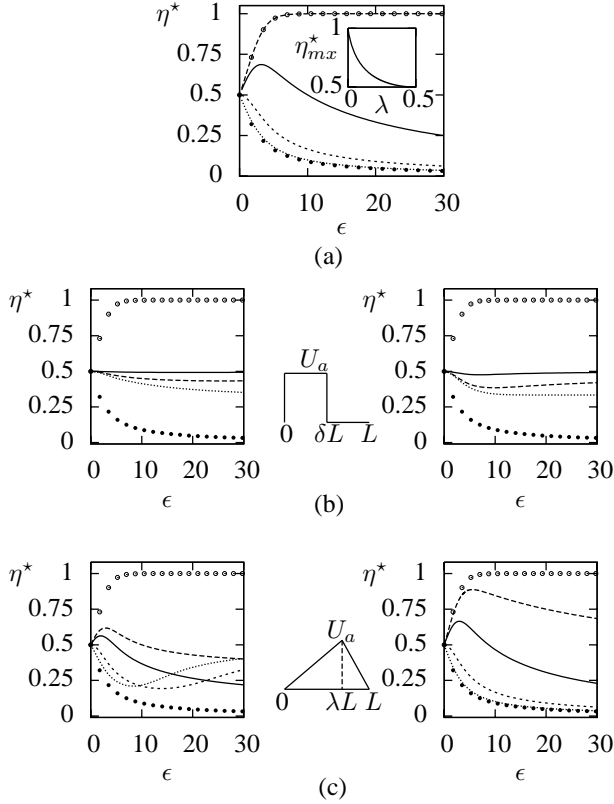


FIG. 2. Efficiency at maximum power, η^* , as a function of net load ϵ . In all panels the open circles represent η_E^* and the filled circles η_K^* . Panel (a): two state model [cf. Eq. (4)] with $\lambda = 0$ (long dashes), 0.1 (solid), 0.5 (short-dashes), and 0.9 (dots). The solid and long-dashed curves exhibit a maximum, clearly seen on this scale in the solid curve, while the two lower curves are monotonic. The inset shows the maximum value of η^* as a function of λ , with $0 \leq \lambda \leq 1/2$. The two panels in (b) are for the periodic square well potential, and those in (c) are for the sawtooth potential. For the former $\delta = 0.1$ in the left panel, 0.5 in the right panel. In both panels, η^* is shown for three barrier heights: $\beta U_a = 1$ (solid), 3 (dashes), and 9 (dots). For the sawtooth potential the curves in the left panel are all for $\beta U_a = 10$ and in the right panel for $\beta U_a = 100$. The four curves are for different values of the potential asymmetry parameter λ : $\lambda = 0$ (long dashes), 0.1 (solid), 0.5 (short dashes), and 0.9 (dots).

Generalized model. The above generic model assumes exponentially difficult crossing of the transition state. With a more general analysis, we suppose that the motion projected on reaction coordinate x can be described as an overdamped one-dimensional diffusion process in a potential $U(x) = U_0(x) - Fx$:

$$\gamma \frac{dx(t)}{dt} = -\frac{dU(x(t))}{dx} + \sqrt{2\gamma k_B T} \xi(t). \quad (7)$$

Here γ is the viscous friction coefficient and ξ is Gaussian white noise, $\langle \xi(t) \rangle = 0$, and $\langle \xi(t)\xi(t') \rangle = \delta(t - t')$. The diffusion coefficient is related to the viscous friction coefficient and the temperature by the Einstein relation

$D = k_B T / \gamma$. This description relates transition rates to more fundamental parameters than the earlier phenomenology. It has been shown to be a very useful tool to describe the response of molecular machines [16], and it has the further advantage of being analytically tractable. It also does not require extremely high activation barriers. Indeed, when the potential barriers are comparable to the thermal energy $k_B T$, it is no longer appropriate to identify the minima of the potential (formerly $x = 0$ and $x = L$) as states between which transitions take place. We therefore replace the two-state scenario by an extended coordinate $x \in [-\infty, \infty]$, and consider a baseline potential $U_0(x)$ periodic in x with period L .

Upon application of a driving force F_1 and a load force F_2 , the net force $F = F_1 - F_2 \geq 0$ induces a steady state current in the tilted potential $U(x) = U_0(x) - Fx$ with average velocity $V = \langle dx/dt \rangle$ along the positive x -coordinate. The transformation of driving energy $\epsilon_1 = \beta F_1 L$ per period into loading energy $\epsilon_2 = \beta F_2 L$ per period takes place at a net rate $k = V/L$, with output power $\Pi = k\epsilon_2 = V\epsilon_2/L$. The efficiency of the transformation is again given by ϵ_2/ϵ_1 , see Eq. (1). We note in passing that, besides being a natural model for cyclic molecular motors such as ATPase, overdamped Brownian motion in a tilted periodic potential also provides a relevant description in a large number of other physical situations [17], including Josephson junctions, rotating dipoles in external fields, particle separation by electrophoresis, transport in tubes of varying cross-section, and biophysical processes such as neural activity and intracellular transport.

Turning to the issue of efficiency at maximum power, we first derive results that hold for arbitrary potential. We suppose that the average velocity V can be written as a power series in F . Since V vanishes for $F = 0$, there is no constant term in the expansion. For comparison with the previous results, we consider the rate $k = V/L$ for moving over one period L , and write the corresponding power series in terms of $\epsilon = \beta FL$, $k = k(\epsilon) = V/L = a_1\epsilon + a_2\epsilon^2 + a_3\epsilon^3 + O(\epsilon^4)$. Maximization of the output power $\Pi = k(\epsilon)\epsilon_2$ with respect to the loading energy ϵ_2 gives the following expansion for the output yield at maximum power [compare with Eq. (3)]:

$$\epsilon_2 = \epsilon - \frac{a_2}{a_1}\epsilon^2 + 2\left(\frac{a_2^2}{a_1^2} - \frac{a_3}{a_1}\right)\epsilon^3 + O(\epsilon^4). \quad (8)$$

The corresponding efficiency reads [see Eq. (5)]:

$$\eta^* = \frac{1}{2} - \frac{a_2}{4a_1}\epsilon + \frac{(3a_2^2 - 4a_1a_3)}{8a_1^2}\epsilon^2 + O(\epsilon^3). \quad (9)$$

This expansion features the familiar 50% efficiency in the regime of linear response. Turning to the nonlinear regime, we note that just as in the generic two state model, the next order correction vanishes ($a_2 = 0$) whenever the system has left-right symmetry for the velocity, $V(F) = -V(-F)$.

The average steady state velocity for overdamped motion in a tilted periodic potential is given by [18]

$$V(\epsilon) = \frac{DL(1 - e^{-\epsilon})}{\int_0^L dx \int_0^L dy e^{\beta[-U_0(x) + U_0(x+y)] - \epsilon y/L}}. \quad (10)$$

This expression in principle allows us to find the power $\Pi = V\epsilon_2/L$, and hence makes it possible to explicitly identify the regime of maximum power and its corresponding efficiency.

Firstly, we rederive the results for the two-state model with a potential U_0 with a dominant high maximum in each period, say at $x = x_a = \lambda L$ (modulo L), and a unique minimum at $x = 0$ (modulo L). The dominant contribution to the double integral in Eq. (10) comes from the region around the (x, y) point for which $U_0(x + y)$ reaches a maximum and $U_0(x)$ a minimum. This point lies at $x + y \equiv x_a = \lambda L$ and $x = 0$, and consequently $y = \lambda L$. The ϵ -dependence of the denominator is therefore of the form $\exp(-\lambda\epsilon)$. It then follows directly that $V \sim k \sim \{1 - \exp(-\epsilon)\} \exp(\lambda\epsilon)$, and the resulting power is identical to that for the two-state model.

Secondly, we note that universal conclusions can be drawn using Eq. (10) even without an explicit evaluation of the integrals. In particular, we can identify the coefficients a_i in Eq. (9),

$$\begin{aligned} a_1 &= \frac{D}{L^2} \frac{1}{I_0}, & a_2 &= \frac{D}{L^2} \frac{2I_1 - I_0}{2I_0^2}, \\ a_3 &= \frac{D}{L^2} \frac{I_0^2 + 6I_1^2 - 3I_0(I_1 + 2I_2)}{6I_0^3}, \end{aligned} \quad (11)$$

where

$$I_n = \frac{1}{n!L^{n+2}} \int_0^L dx e^{-\beta U_0(x)} \int_0^L dy y^n e^{\beta U_0(x+y)}. \quad (12)$$

Since $0 \leq I_1 \leq I_0$, the coefficient $a_2/4a_1 = (I_1/I_0 - 1/2)/4$ of the linear term lies between $-1/8$ and $1/8$, as was the case for the 2-state model, see Eq. (5). Furthermore, the coefficient is zero for a potential with left-right symmetry, that is, when there exists a point x_0 for which $U_0(x - x_0) = U_0(x_0 - x)$.

To proceed further, it is in general necessary to invoke numerical calculations because the integrals in (10) can not be performed analytically for a general potential $U_0(x)$. However, analytic results can be obtained in some limits (such as the dominant high maximum case considered above), or for some specific shapes of the potential. Examples include the square well, $U_0(x) = U_a$, $x \in [0, \delta L]$ modulo L , and $U_0(x) = 0$, $x \in [\delta L, L]$ modulo L , and a saw-tooth potential. To illustrate, we quote the ef-

ficiency at maximum power for the square well potential,

$$\eta^* = \frac{(e^\epsilon - 1)}{(e^\epsilon - 1)(3 + \epsilon\zeta) + \epsilon}, \quad (13)$$

$$\zeta = \frac{\epsilon(e^\epsilon - 1) + c[1 + e^\epsilon + e^{(1-\delta)\epsilon} - e^{\delta\epsilon}]}{(1 - \epsilon - e^\epsilon) + c[1 - \delta e^{(1-\delta)\epsilon} + (\delta - 1)e^{\delta\epsilon}]},$$

where $c \equiv 4 \sinh^2(\beta U_a/2)$. The efficiency η^* for the square-well and sawtooth potentials are shown in Figs. 2(b) and (c).

Finally, we mention a generic behavior for any potential with finite maxima. For very large driving, the barrier(s) of the potential U_0 , indeed the entire potential, become irrelevant and one goes back to a linear model with $V = F/\gamma = a_1\epsilon$ with $a_1 = D/L$, implying that $\eta^* = 1/2$. This return to the linear scenario can be seen in some cases in Fig. 2; in others one must go to higher values of ϵ than those shown in the figure.

Closing perspective. Is the issue discussed in this paper, maximizing power with respect to the load, a relevant criterion in practice? In the case of thermal motors, this seems to play a role, at least from an engineering point of view, since power plants operate under conditions in general agreement with this criterion [11]. We hope that the present paper will lead to a re-examination, from the perspective of maximum power, of the much larger class of isothermal engines, including the important class of molecular motors.

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